SILVER SAMPLES MELTED IN SPACE
SKYLAB EXPERIMENT M565

By

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SUMMARY

The objective of the experiment was to make a preliminary study of the behaviour of porous material when melted and resolidified in weightless condition.

Two kinds of samples have been used: perforated discs and a fibre compact. The observations made on the various specimens are presented and compared with those made on similar specimens treated in the same manner on the ground.

Some provisional conclusions are:

(1) most of the original porosity in the samples has disappeared during the melting stage. This could possibly be avoided by different heating and pressure conditions or by using samples with closed pores. If necessary, the mobility of the pores could probably be reduced by the presence of a slowly diffusing gas

(2) even if samples were perfectly spherical in the liquid state, their shape is altered on solidification due to both shrinkage pipe formation and constitutional supercooling

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(3) the leveling out of impurity concentration gradients appears indeed to be slow in the molten metal when gravity induced convection is absent

(4) when only a part of a solid body is melted in zero gravity, the tendency of the molten part to become spherical may be much restricted.

OBJECTIVES OF THE EXPERIMENT

Some products made by powder and fibre metallurgy are intentionally porous, e.g., self-lubricating bearings, filters and damping devices. When a high porosity is desired, the necessary cohesion of the material can only be obtained through solid phase sintering, as any substantial melting would cause a rapid collapse of the porous structure. However, this may no longer happen when the melting is done in weightless condition. The melting of a porous material in space may produce a porous part in which size, shape and distribution of the pores are different from those obtainable on earth by classical powder metallurgy. Hence, some properties of the material, such as strength or filtering characteristics, may also be different from those that have been obtained so far. Knowledge gained through melting and resolidifying experiments on porous material in space, may therefore promote the development of new materials or the development of space techniques, e.g., repairing porous spacecraft parts by welding in space.

EXPERIMENTAL

The furnace

The Skylab multipurpose furnace M 518, designed and built by Westinghouse, can contain three stainless steel cartridges in which the specimen containing ampoules are sealed in (fig.1-3).
The main characteristics of the furnace are:

- outside diameter: about 10 cm
- overall length : about 30 cm
- powder of resistance heater: 150 watts
- maximum temperature: about 1000°C
- length of hot zone: 5 cm
- length of gradient zone: about 6 cm
- length of heat extraction zone: about 15 cm
- inner diameter of each of the three experiment chambres: about 2cm

The temperature is measured by two thermocouples located one in the graphite heat leveler, which separates the heater resistance from the experiment chamber, and the other in the heat extractor plate.

The cartridges

The cartridges (fig.4) were also designed and manufactured by Westinghouse. For the silver melting experiment they were made such as to provide a small temperature gradient in the hot zone. The purpose was that a part of the samples would not melt. This appeared to be the only way to be sure that the temperature had not exceeded too much the melting temperature, as the actual temperature of the samples could not be measured. Moreover, a varying temperature might yield additional information.

It had been anticipated to conduct the heating in such a way that the part of the samples which should melt, would stay only a short time at temperatures at or slightly above the melting point.

However, the ground based tests, made on similar samples and in a similar furnace as those used in flight, showed that the furnace had to be set on maximum power during heating up, and that there had to be a soak for one hour at the maximum allowed temperature in order to melt a little more than half of the samples. Because of these experimental limitations the most interesting experimental conditions such as very short holding times just above the melting point could not be obtained.

The ampoules

For the ampoules which had to contain the samples, the choice fell on silica tubes sealed in vacuo and designed in such a way (fig.5) that the various parts inside the ampoule were held together by a silica piston firmly enough as to avoid rattling. In fact rattling has not been avoided completely in every case, but this has not caused any serious trouble.

The samples

It appeared sensible to start with experiments on samples which are easy to characterise, at least in some ways. Originally it was intended to use two- and three-dimensional grids made of silver fibres arranged in regular arrays, as shown in fig.6. The possible variables were: wire diameter, mesh size, number of stacked layers, melting temperature, duration of melting and atmosphere (pressure). From melting and resolidifying such samples in space a wide variety of product shapes could be expected, ranging from many small spheres to a single massive sphere with in between various intermediate configurations.

When it became known that each experiment which NASA accepted for the Skylab furnace would have to be performed in a single run,

- i.e. that only one maximum furnace temperature and only one duration would be available, a drastic redesign of the experiment has to be made. A set of samples was finally selected as described below. The choice was also affected by the circumstance that a small temperature gradient would be provided in the high temperature zone of the furnace.

Silver was chosen as the experimental material because it is a typical metal, readily available with high purity, fairly unexpensive, easy to roll and draw, and melting at a temperature (961,9°C) below the maximum available temperature of 1000°C. The silver was of 99,999% grade (electrolytic silver melted under hydrogen in graphite crucible).

The ampoules were loaded as follows:
Ampoule A (fig.5) contained 8 silver discs of 14 mm diameter and 0.1mm thickness in which one or more holes had been spark cut or drilled as follows, when counting from the hot end of the ampoule:
P8: 1 central hexagonal hole of 3.5 mm side
P7: 1 central hexagonal hole of 3.5 mm side
P6: 1 central square hole of 1 mm side
P5: 4 square holes of 1 mm side and 6.4 mm apart
P4: 9 round holes of 1 mm diameter and 3.2 mm apart
P3: 21 round holes of 1 mm diameter and 1.6 mm apart
P2: 14 round holes of 2 mm diameter and 0.8 mm apart
P1: 21 round holes of 2 mm diameter and 0.4 mm apart

The silver discs were held apart by silica ring spacers and, in order to avoid mixing of the melting products from different discs, the silica ampoule was divided in compartments by stainless steel grids. The silica ampoules were sealed under a vacuum of about 10^{-5} mm Hg. Before sealing they were heated for one hour at 350°C in the same vacuum in order to decompose any Ag_2O present.

Ampoule B had exactly the same load as ampoule A, except that the discs had a thickness of 0.5 mm.

Ampoule C (fig.7) contained a single sample made of silver fibres of 0.4 mm diameter and 10-15 mm length. The fibres had been poured as randomly as possible into a cylindrical die, compressed into a disc of about 4 mm high and 50 mm diameter (maximum pressure about 10 kg/mm^2). The disc was sintered in hydrogen for two hours at 900°C. From this disc a prism was cut to dimensions 40 x 14 x 4 mm. The porosity was 30% for the Skylab sample and 33% for the ground based test sample.

The temperature

Fig.8 shows the uncorrected temperature-time curves for the actual Skylab experiment. The hot thermocouple rose from 35°C to its maximum 1035°C in 3 1/2 hours and remained for 1 hour at the maximum temperature, when the power was cut off. The initial passive cooling rate was 38°C for the first five minutes.

The exact thermal history (temperature of the samples themselves versus time) is not known. Especially for the fibre sample the time spent above the melting point may have been short because the molten part was sucked down the temperature gradient by the unmolten part as a result of surface tension.

RESULTS AND DISCUSSION

Plate specimens

Fig.9 shows radiographies taken from three different angles at 120° of the plate samples after the Skylab and ground experiments and before taking them out of the ampoules. In both Skylab ampoules (1A and 1B) five out of the eight plates melted, whereas in the ground

ampoules either four (3A) or five (3B) plates melted.

The Skylab samples which did melt are obviously more spherical than the ground samples, except one which remained in contact with a silica ring and wetted it. They are not complete because during solidification, due to small accelerations in Skylab, there was local contact, with limited wetting, with the stainless steel grid. In one instance (1B) two molten spheres must have come into contact with each other through the holes in the steel grid and one of them has sucked the other one right through the grid so that both spheres have united into one.

All the molten plates of 0.5 mm thickness have each turned into a single droplet of molten metal. On the contrary, of the plates of 0.1 mm thickness some have become one droplet and others have split into several small droplets. Model calculations are being made in order to attempt an interpretation of this result. It is unfortunate of course that the plates containing many holes (14 or 21) could not be melted.

An examination of the B samples with the scanning electron microscope shows that, even if they had had no contact during solidification with neither the stainless steel nor the silica, the spheres would have been far from perfect. This is shown by figs.10 (sample 1B P7-8) and 11 (sample 1B P6). Even if the spheres have been perfect in the liquid state, on solidification a network of grooves has appeared on their surface and a shrinkage pipe has been formed. The grooves are the traces of a cellular solidification substructure. Cellular solidification has been found in many systems, although observations are generally made on decanted solid-liquid interfaces (1,2). The cell formation is attributed to constitutional supercooling which itself is due to impurities which segregate to or from the cell boundaries (e.g. 20 ppm lead in tin).

In the present case, according to the manufacturer of the silver, any impurity in the ingots used has a concentration less than 1 ppm, except iron which is less than 1,5 ppm. The plate specimens had been made from these ingots by cold rolling and they were not heated until the degassing treatment just before sealing the ampoules. Nevertheless, it appears likely that at least the surface of the silver has been contaminated with oxygen, iron and other elements by contact with various products, such as tools, lubricants, cleaners, atmosphere (before and after sealing), stainless steel grids (after melting). Although the total contamination must be very low, the cellular substructure reveals the presence of impurities at least near the surface.

Similar traces of cellular substructure have been found on the ground tested specimens (fig.12). However, there the grooves are confined to a small region which was obviously the last to solidify (fig. 13). On the contrary, in the Skylab samples the grooves appear to occur all over the surface of the samples (fig.10 and 14), indicating that solidification has progressed in a different way.

It has been checked by X-ray diffraction that regions where a substructure is clearly visible, are monocrystalline with small disorientations.(fig.15).

The density of the samples has been measured to check if internal pores are present. The results are inconclusive. The samples are now being cross sectioned by gradually polishing away thin layers of material.

It is concluded that cellular solidification and shrinkage pipe formation may easily prevent the obtention of perfect spheres by melting and solidification in zero gravity. In principle, cellular solidification can be avoided by increasing the purity of the metal or by

increasing the temperature gradient in the solidifying melt. Pipe formation can also be controlled by the thermal conditions. Further study would be necessary to find out if both disturbing factors could be completely eliminated.

Fibre specimens

Figs. 16 and 17 show different views of the Skylab and the ground test melted fibre specimens. The amount melted in both cases is nearly the same, so the temperature distribution should have been very much the same in both experiments.

The ground test specimen stood upright during the test, hot end above, and the molten metal ran down the unmelted part and took the cylindrical shape imposed by the quartz half cylinders. On the contrary, the molten part of the Skylab specimen (henceforth called "the bead") did not touch any solid material except the unmelted part of the specimen: its shape is therefore determined by surface tension and by the constraints due to the shape of the unmolten metal. An attempt is being made to calculate the shape of the "bead". The shape of the "shoulders" (fig.17) between the solid and the molten silver appears to be similar in both specimens. In fact, the contact angle between solid and liquid silver is zero, but in the present case the spreading out of the liquid silver was halted by the temperature gradient.

In the Skylab specimen traces of the individual fibres can apparently still be distinguished on the entire surface of the "bead". Details of this surface can be seen on fig.18. It is suggested that the fibre traces are akin to the grooves observed on the plate specimens and that they also are due to impurities. Notwithstanding

the sintering in hydrogen and the heating in vacuo before sealing the ampoules, the fibres must have a surface layer enriched in impurity atoms. When the fibres melt and merge together, their impurity-rich surfaces can persist for some time in the pool of liquid, owing to the absence of gravity induced convection. Apparently such segregation of impurity atoms still existed when the metal solidified and gave rise to the traces or grooves visible all over the outer surface of the bead. Fig.19 shows small holes in such a groove, presumably due to the rejection of oxygen from the liquid. Such traces are not visible on the ground tested specimen even on the solidified surface which was not in contact with the silica, neither have they be seen on other specimens melted on earth without contact with crucible material. It is concluded that diffusion and surface tension induced convection (Marangoni effect) are much slower than gravity induced convection in equalizing concentration variations.

The central part of the bead (when seen in profile), corresponding to the original thickness of the sample, has a blackish appearance. There the surface is essentially made up of cross-sections through fibres. The black appearance seems to be due to small silver spheres (diameter 1-10 μ), which condensed from evaporated metal (fig.20). Condensed crystals have also been found on the silica tube walls but there they have a more faceted appearance (fig.21).

Fig.22 shows a longitudinal as-cut section parallel to the thickness direction of respectively the Skylab and the ground test sample. The section was made by very slow spark cutting, using a 0.5 mm diameter tungsten wire as electrode. The cutting speed was kept as low as about 0.1-0.2 mm/hour in order to minimize surface damage.

The ground sample shows some residual porosity mainly in the central part. There the metal did not melt as is shown by the irregular shape of the pores. In the outer regions the silver did melt and run down and only a few rounded pores are left. This has been confirmed by electrolytic etching (fig.23): the grains in the molten part are very large and without twins, those in the unmelted region are small and full of annealing twins. The etching has also revealed that the surface has been damaged only slightly by the cutting: some holes got covered by a thin film of material which is removed by the etching.

The Skylab sample (fig.24) shows a quite small residual porosity, and the pores are not necessarily spherical although the bead completely melted, as has been checked by etching (fig.25). Besides the few larger pores (diameter 0.1-1mm) seen in figs. 24-25, many small pores are also present (sizes 0.01-0.1mm) both on grain boundaries and inside grains (fig.26). Because of their rounded shape they can be identified as gas holes, not as shrinkage cavities. The observed (small) porosity can probably be explained as follows.

First of all it appears likely that only a few pores got trapped in the melting silver. Indeed, just below the "bead" the outside dimensions of the specimen (length and width of the cross-section) have not changed. Yet, the porosity has much decreased. This shows that liquid metal has infiltrated from the bead and has solidified on the still unmelted fibres, the twinned crystals of which have grown into the liquid. From this it can be inferred how the melting of the fibre specimen has actually occurred. Owing to the temperature gradient, the melting has of course started at the hot end (the top in the figures shown). As soon as some metal melted, it flowed into the open pores between unmelted neighbouring fibres which melted themselves a little later and provided liquid to fill the pores in the next layer. In this way only few pores got trapped in the liquid.

The few pores which were entrapped should have adjusted their size so as to fet equilibrium between the enclosed gas pressure and the surface tension restraint $p = \frac{2\gamma}{R}$, in which is the surface tension and R the pore radius. A pore of initial radius R_1 at a gas pressure p_1 should shrink or expand to a radius R_2 given by

$$R_2 = \left(\frac{p_1 R_1^3}{2\gamma}\right)^{1/2}$$

In the present case it can be taken that $p_1 = 4.10^{-5}$ mm Hg (taking into account the pressure increase by a factor four on heating from room temperature to the melting point of silver) and γ = 1000 dyne/cm.

Assuming that the entrapped pores had an original diameter of 1 mm or less the above formula shows that they should shrink to a diameter of 10^{-3} mm or less. This result is not so much influenced by a substantial decrease of the surface tension (such as due to impurities) or by using an initial pressure of, say one order of magnitude higher. It is concluded that pores entrapped on melting have become extremely small or have coalesced or left the metal while it was in the molten state. Indeed, even in the absence of gravity induced buoyancy and convection, pores in a liquid specimen may move because of surface tension induced convection, and they will tend to coalesce and to move to the free surface because of diffusion. Coalescence of pores in a weightless liquid is similar to the so-called Ostwald ripening or coarsening of a fine precipitate in a solid metal or to the coarsening of gas filled pores in solids (3). In these cases a small gas hole or second phase particle is gradually dissolved and reprecipitated on a larger pore or particle, simply because the solubility in the solid increases with the curvature of the interface. Such a process is either diffusion or interface controlled.

It has been concluded above that surface induced convection and diffusion appear to be relatively slow. Consequently, although it is not known how long the "bead" was actually molten (upper limit 1 hour), it seems improbable that all pores visible are residual porosity which persisted from melting till solidification. The size and distribution of the smaller pores suggest that they at least are rather due to dissolved oxygen being rejected from the liquid on solidification. The density of small gas holes is less near the free surface of the specimen where the gas could escape more easily. This kind of pores is much less frequent in the ground test sample, where buoyancy made them move faster than the solidification front at which they formed.

Besides the rounded gas holes there may be a few less rounded micro-shrinkage holes. Near the top of the bead there are two irregularly shaped cavities which apparently are shrinkage holes: they lie in the zone which was the hottest and the last to solidify.

The contour of the longitudinal section of the bead is fairly irregular which corresponds to the rather rough appearance of the outer surface of the bead as described above.

SUMMARY AND CONCLUSIONS

The examination and study of the experimental results is not yet finished. Some samples, such as the A series (thin plates), have still to be examined in detail. The presence and distribution of impurities in all specimens has to be checked. An attempt is being made to calculate theoretically the shape of the various specimens after melting and solidification. Moreover, other experiments should be performed. Therefore, the following conclusions are only provisional:

1. Most of the original porosity in the samples has disappeared during the melting stage. This has been favoured by the fact that the pores were of the open type, by the presence of a temperature gradient and by the low pressure. It should be possible to obtain a more porous product when starting from a material with gas filled closed pores, and if the stay above the melting point is not long enough to allow the pores to coalesce and to migrate to the free surface by diffusion and surface tension induced convection. Even with samples with open pores such as those used in the present investigation, the obtention of a porous product might be possible if the heat input was the same on all sides of the specimen so that a molten surface layer would enclose the still unmelted material. As regards the way in which the geometry of a porous specimen (e.g. a grid) changes with time on melting in weightless condition, one should perform experiments using levitation melting and high speed image recording.

2. The experiment has shown that the shape and surface condition of a sample melted and solidified in space is not only determined by surface tension: shrinkage may cause the formation of a pipe and constitutional supercooling, caused by impurities, may result in a cellular substructure leading to a network of grooves on the surface. These disturbing factors might be reduced by modifying the thermal conditions and by increasing the purity of the metal or avoiding any contamination.

3. The leveling out of concentration gradients, as may be caused by pick up of the impurities at the surface, appears to be slow in the molten metal when gravity induced convection is absent. Therefore the action of diffusion and of convection due to variations in surface tension, appears to be slow.

4. When only a part of a solid is melted in zero gravity, the tendency of the molten part to become spherical can be much restricted. This would be important for applications such as zone melting in space and welding of porous or massive material in space.

It is clear that the experiment performed in Skylab is only a crude and preliminary approach to the problem area outlined in the introduction of this report.

It is hoped that Spacelab will provide the opportunity to carry out more melting experiments on silver or other metal samples under conditions different from those available or applied in Skylab. It would e.g. be interesting to use levitation melting and high speed image recording so that the changes of shape during the whole process can be observed.

ACKNOWLEDGEMENTS

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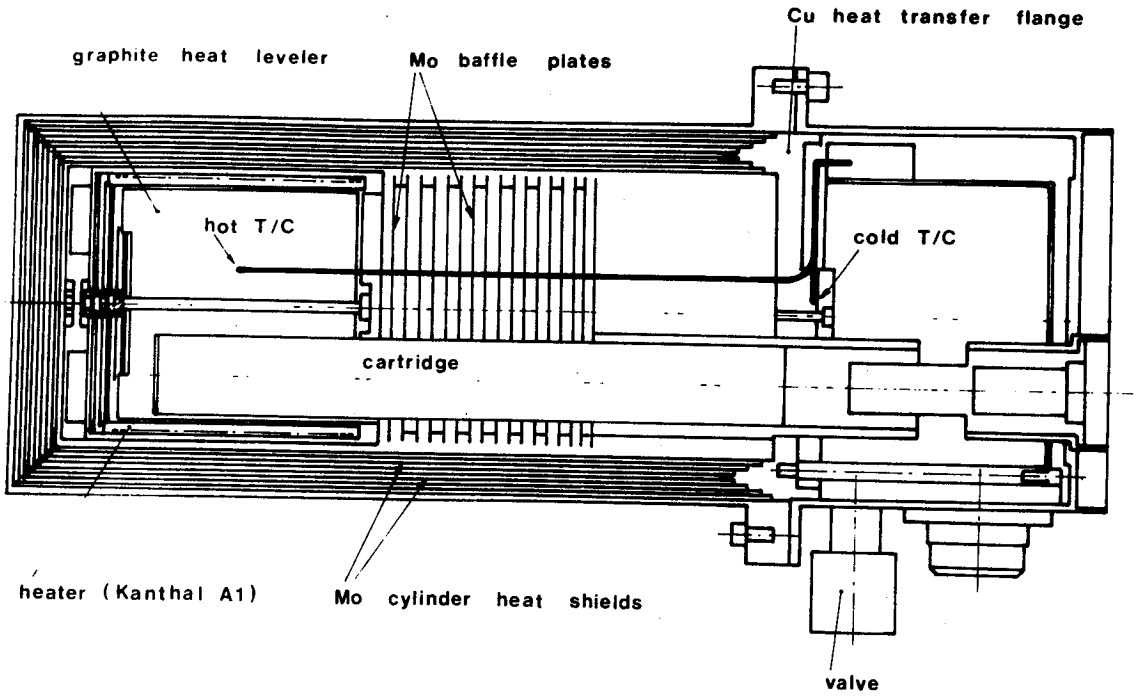


FIGURE 1. MULTIPURPOSE ELECTRIC FURNACE (SCHEMATIC)

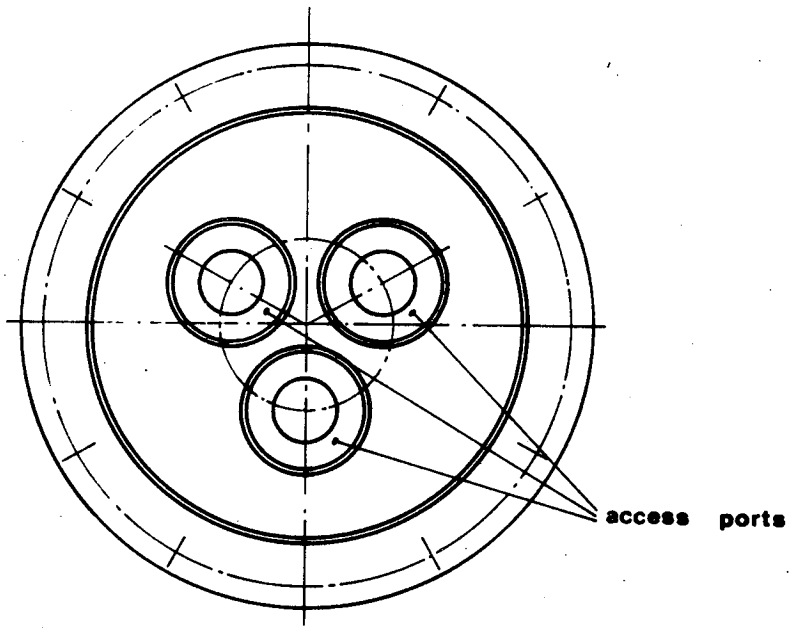


FIGURE 2. FRONT VIEW OF THE MULTIPURPOSE ELECTRIC FURNACE (SCHEMATIC)

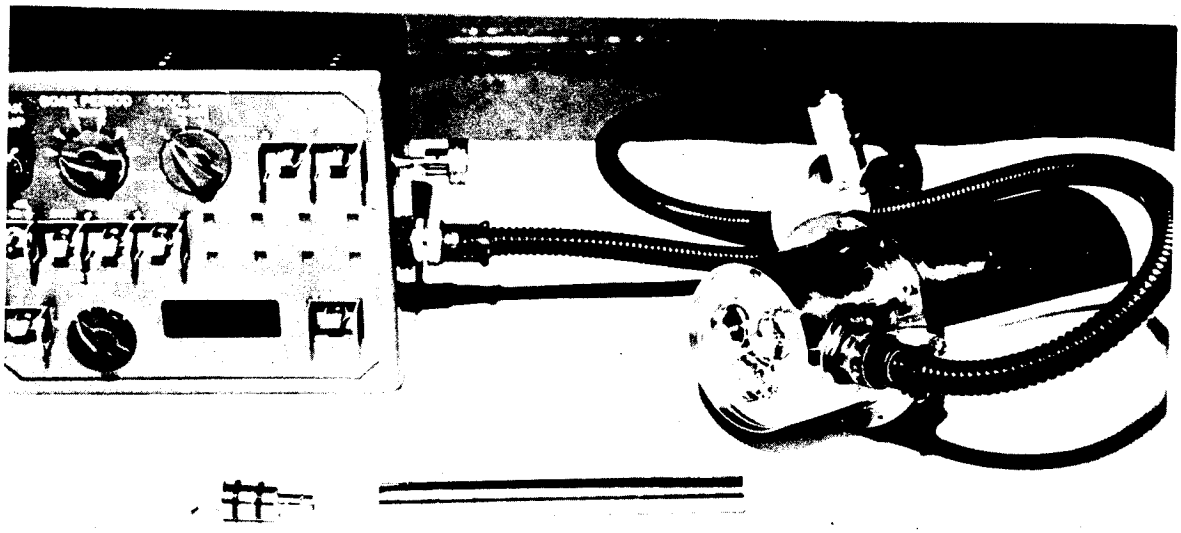


FIGURE 3. SKYLAB EXPERIMENT M518 MULTIPURPOSE ELECTRIC FURNACE

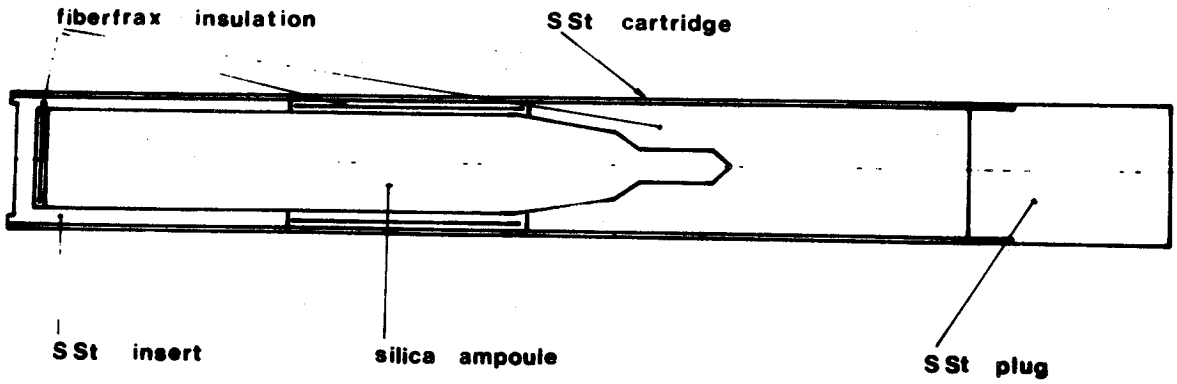


FIGURE 4. EXPERIMENT M565 CARTRIDGE ASSEMBLY
(SCHEMATIC)

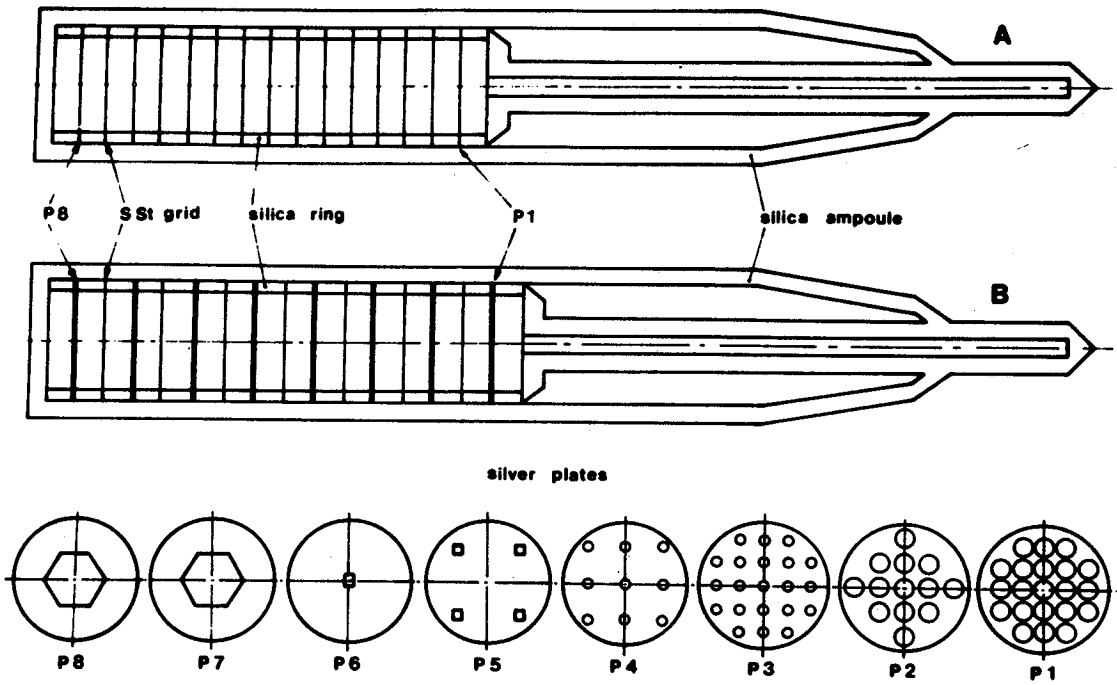


FIGURE 5. AMPOULES A AND B WITH PLATE SPECIMENS (SCHEMATIC).

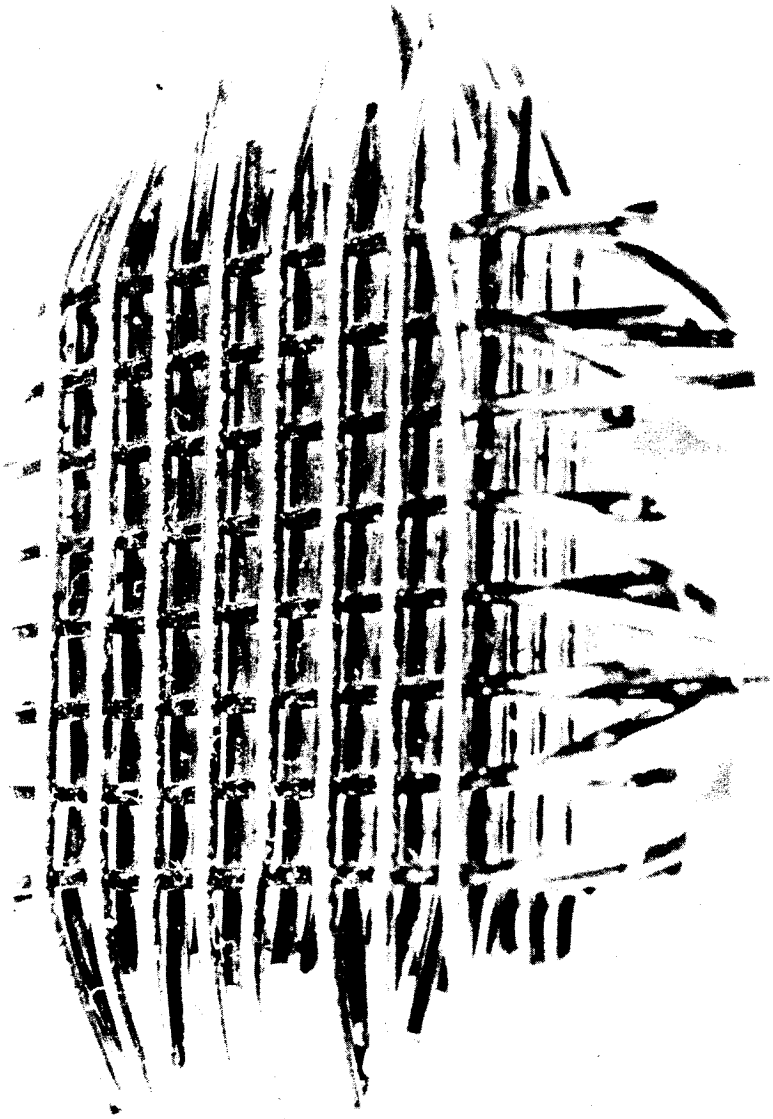


FIGURE 6. MULTI-LAYER SILVER GRID.

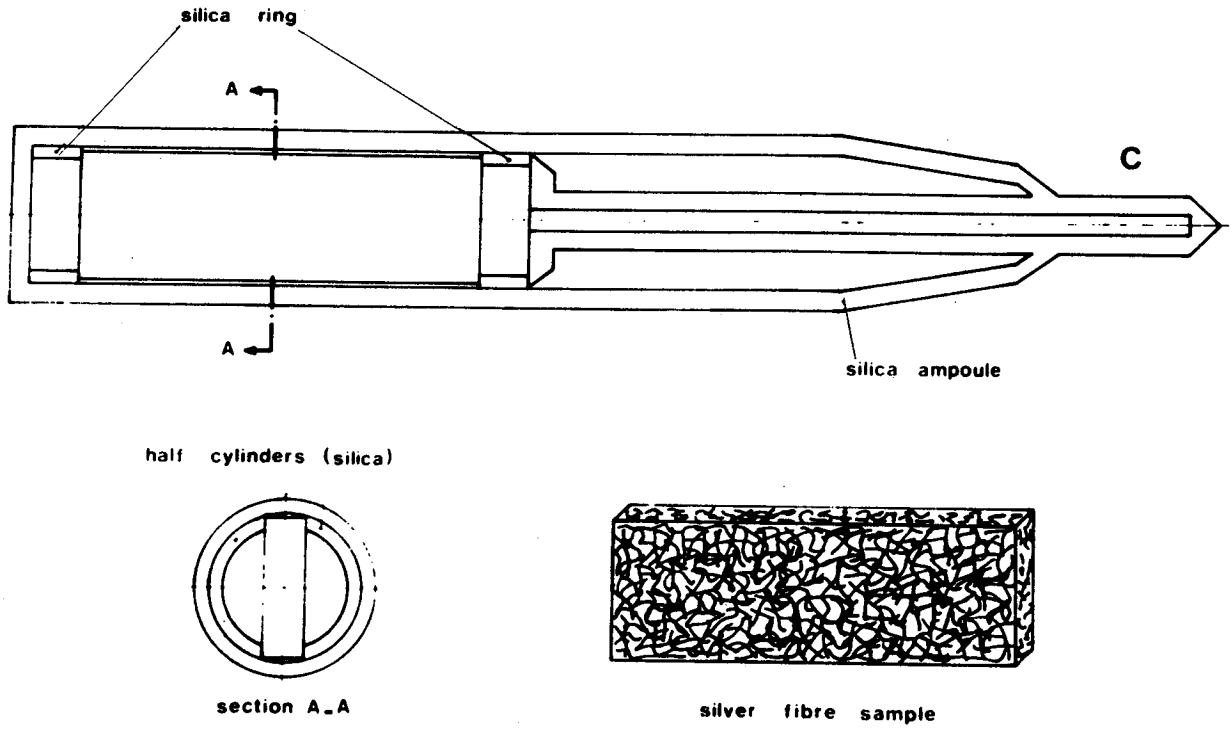


FIGURE 7. AMPOULE C WITH SPECIMEN (SCHEMATIC).

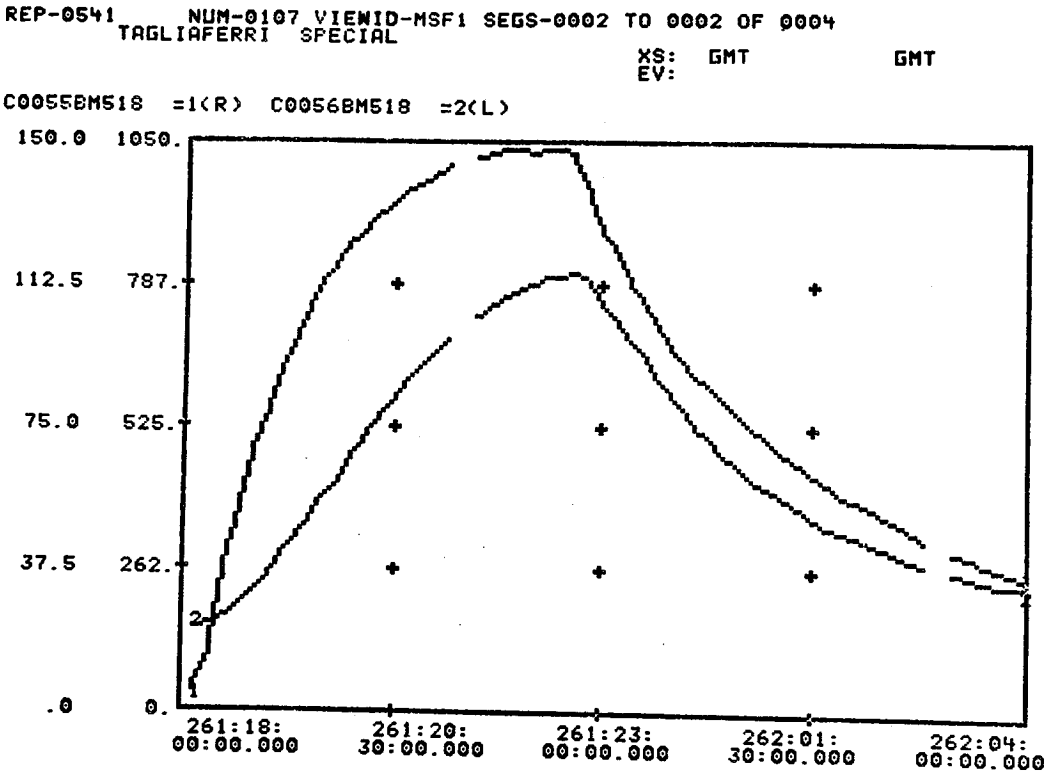


FIGURE 8. TEMPERATURE-TIME CURVES FOR THE ACTUAL SKYLAB EXPERIMENT. CURVES 1 AND 2 SHOW RESPECTIVELY THE HOT AND COLD THERMOCOUPLE READINGS.

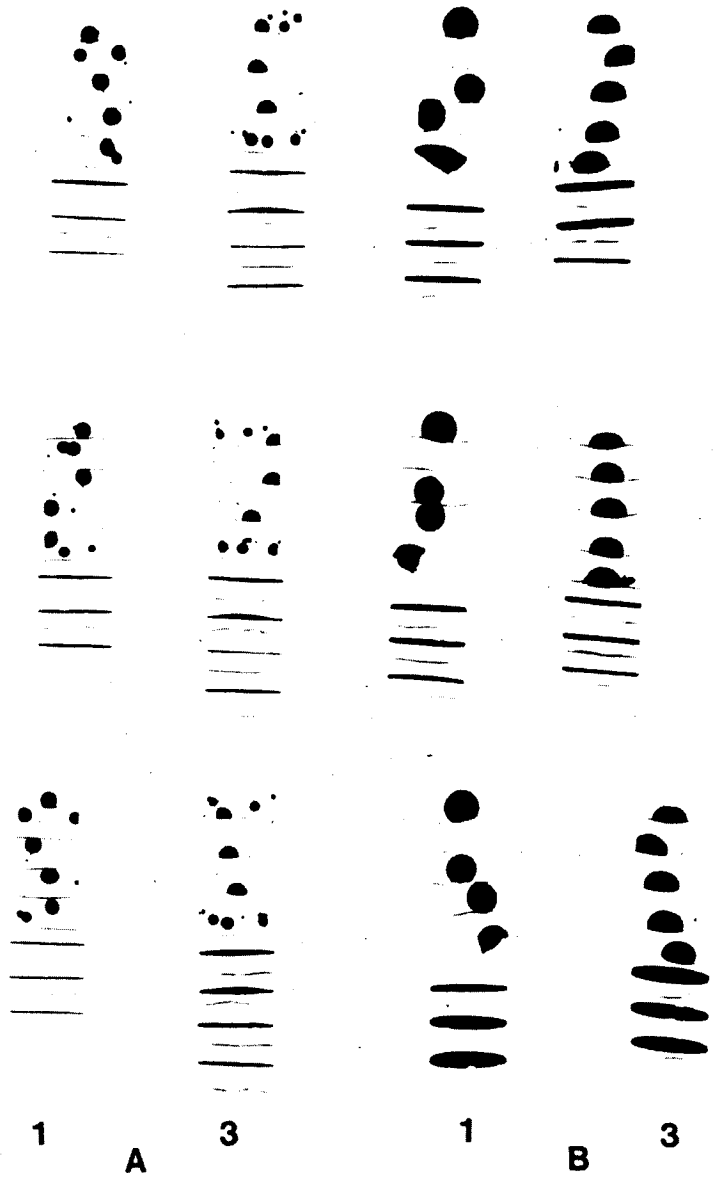


FIGURE 9. RADIOGRAPHIES OF THE SKYLAB (1A AND 1B) AND GROUND (3A AND 3B) TESTED SAMPLES IN THEIR UNOPENED AMPOULES. THREE RADIOGRAPHIES AT 120° OF EACH AMPOULE.

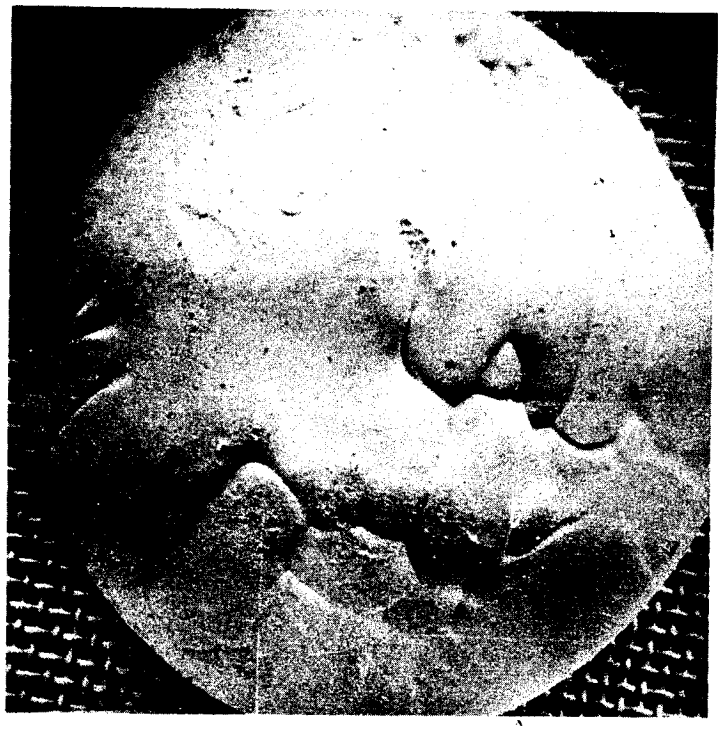


FIGURE 10. SKYLAB SAMPLE 1B P7-8 SHOWING CELLULAR SOLIDIFICATION SUBSTRUCTURE (X 20)

FIGURE 11. SKYLAB SAMPLE 1B P6 SHOWING PIPING AND SUBSTRUCTURE. (X 92)

FIGURE 12. GROUND SAMPLE 3B P4 SHOWING CELLULAR SOLIDIFICATION SUBSTRUCTURE (X 45)

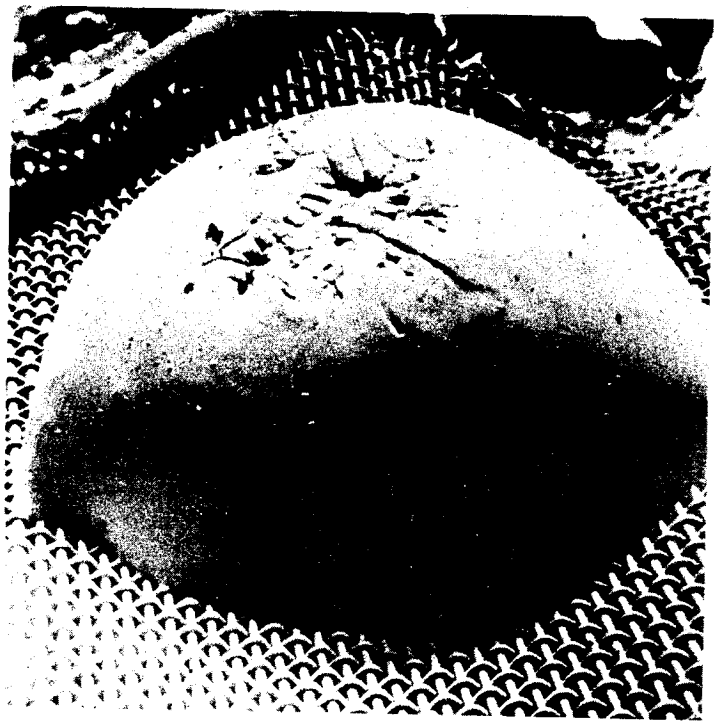


FIGURE 13. GROUND SAMPLE: SUBSTRUCTURE IS LOCALIZED (X 20)

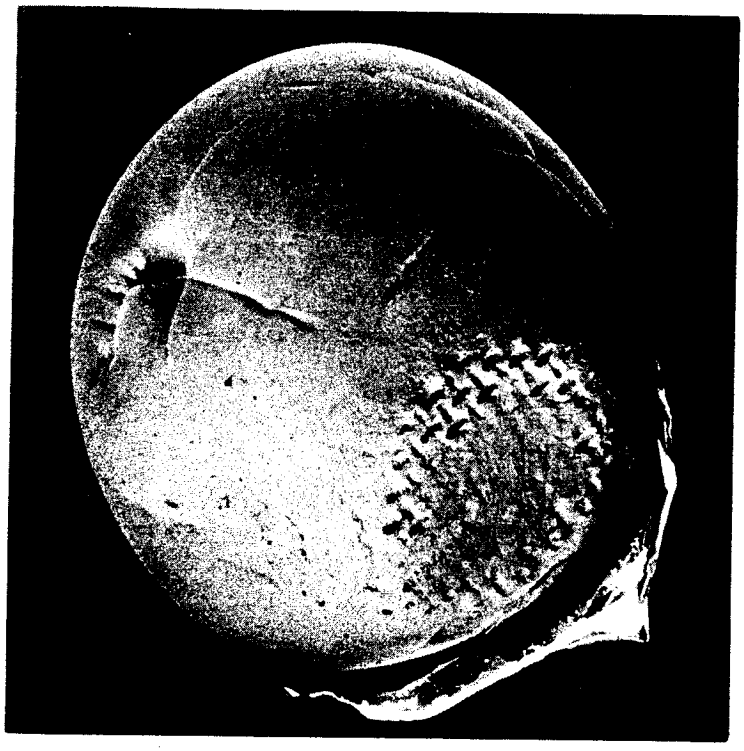


FIGURE 14. SKYLAB SAMPLE: SUBSTRUCTURE IS GENERALIZED (X16)

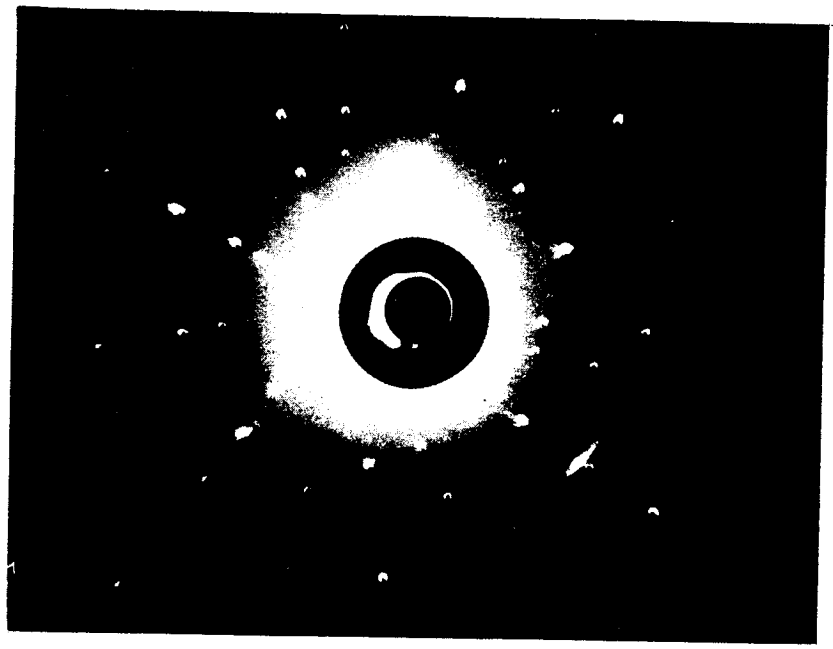


FIGURE 15. LAUE BACK REFLECTION PHOTOGRAPH OF SKYLAB SAMPLE 1B P6 (REGION SHOWN IN FIGURE 11)

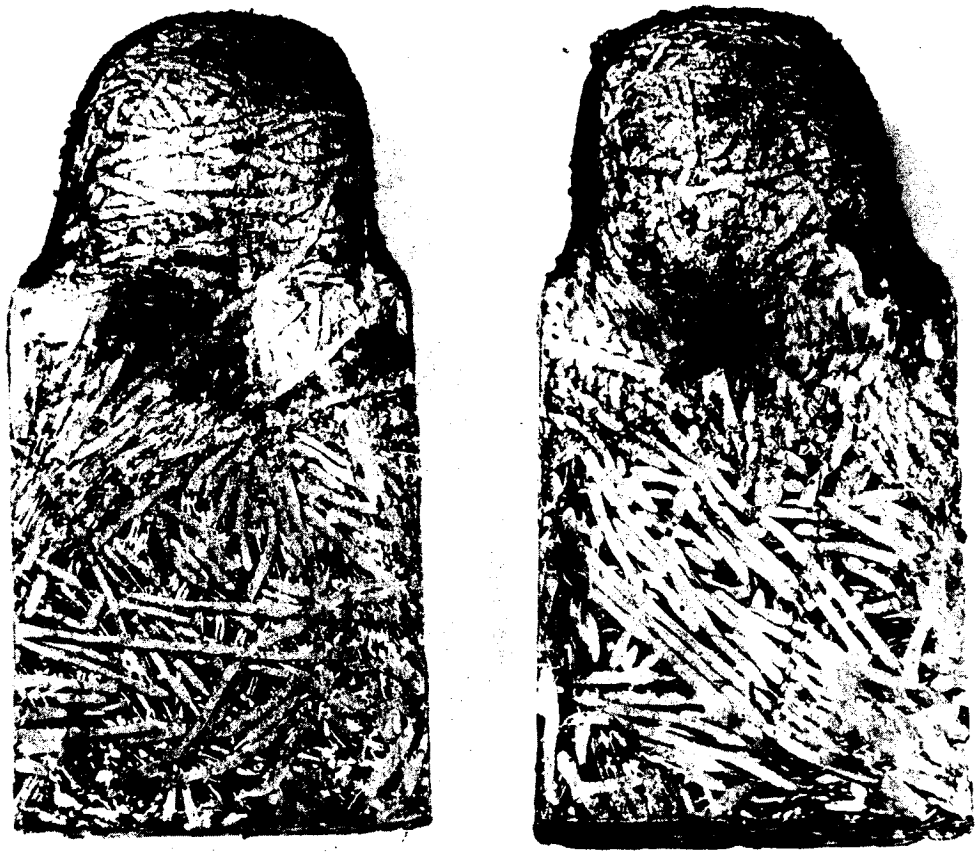


FIGURE 16a FRONT AND BACK VIEW OF SKYLAB TESTED FIBRE SPECIMENS. VERY APPARENT FIBRE TRACES ON "BEAD" OF SKYLAB SPECIMEN.

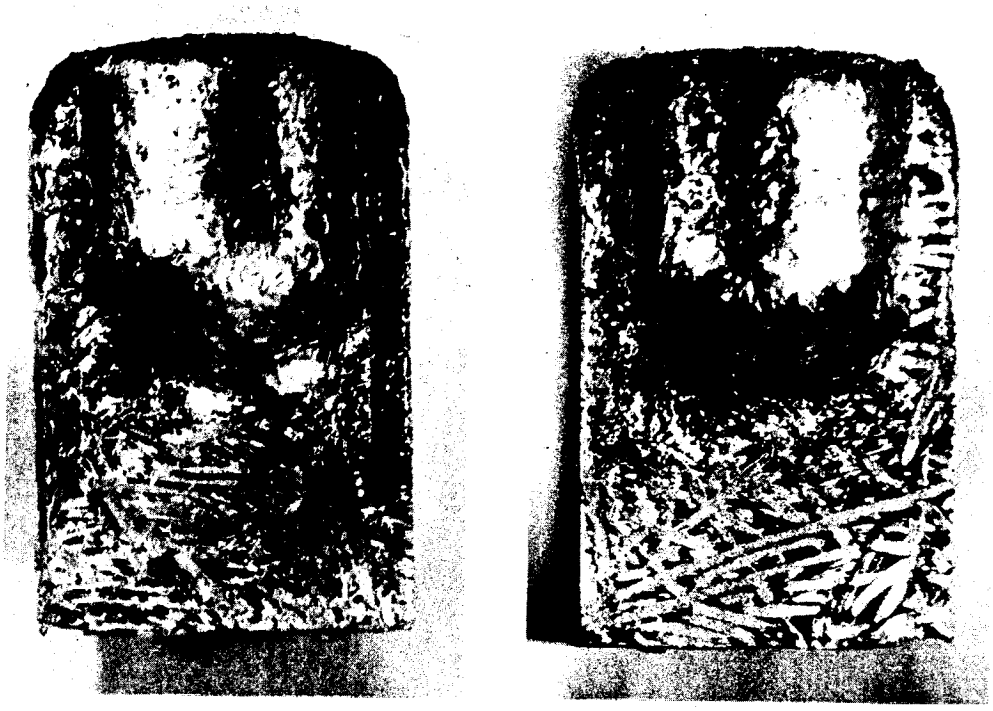
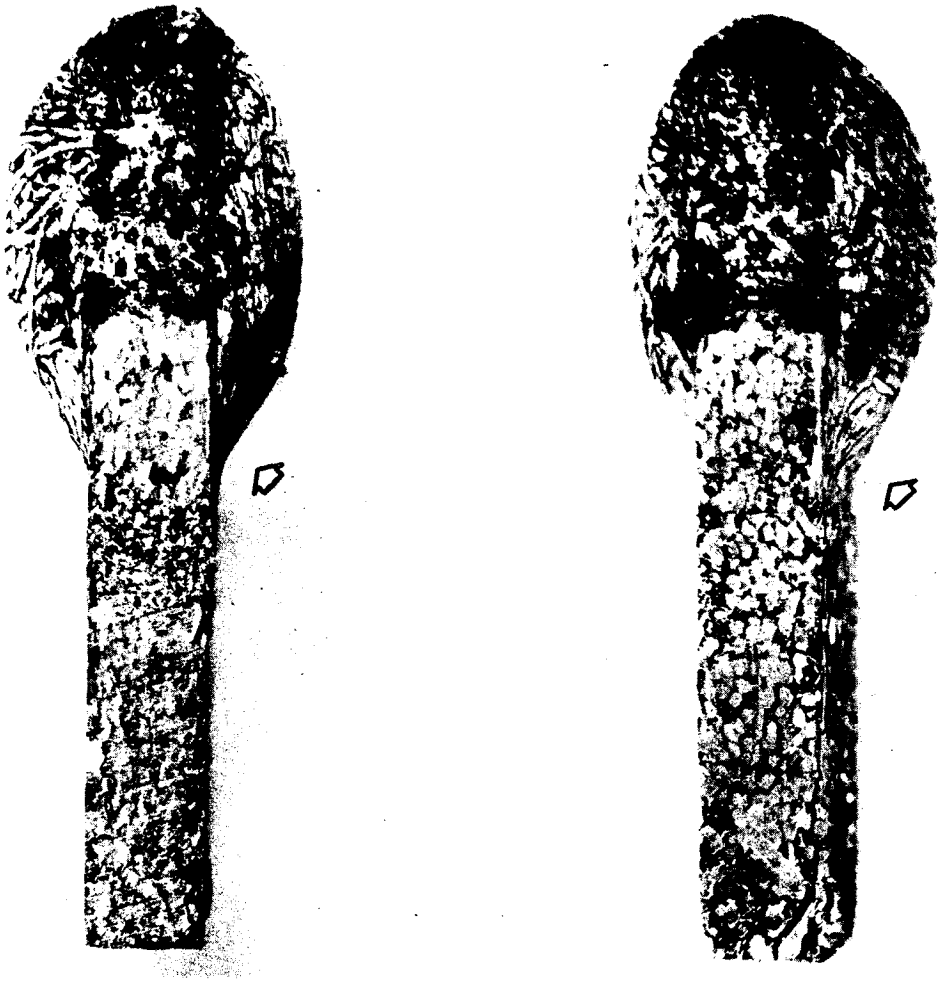
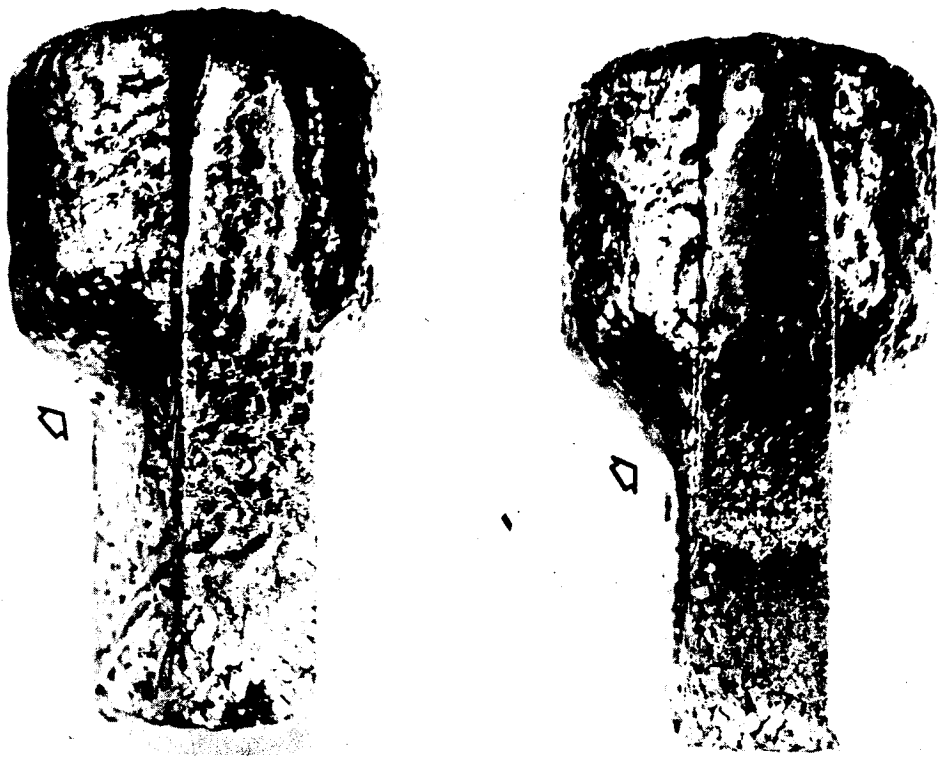


FIGURE 16b FRONT AND BACK VIEW OF GROUND TESTED FIBRE SPECIMENS.



◊ = shoulders

FIGURE 17a. SIDE VIEWS OF SKYLAB TESTED FIBRE SPECIMENS.



◇ = shoulders

FIGURE 17b. SIDE VIEWS OF GROUND TESTED FIBRE SPECIMENS.

FIGURE 18. SKYLAB MELTED FIBRE SPECIMEN (X 5).

FIGURE 19. GROOVE IN SKYLAB MELTED FIBRE SPECIMENS (X 1100).

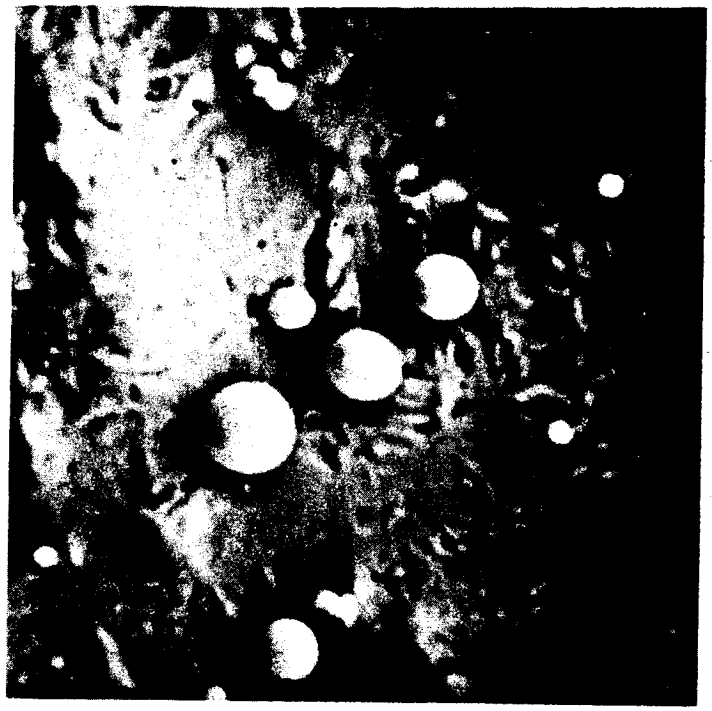


FIGURE 20. SILVER SPHERES CONDENSED ON SKYLAB MELTED FIBRE SPECIMEN (X 1300).

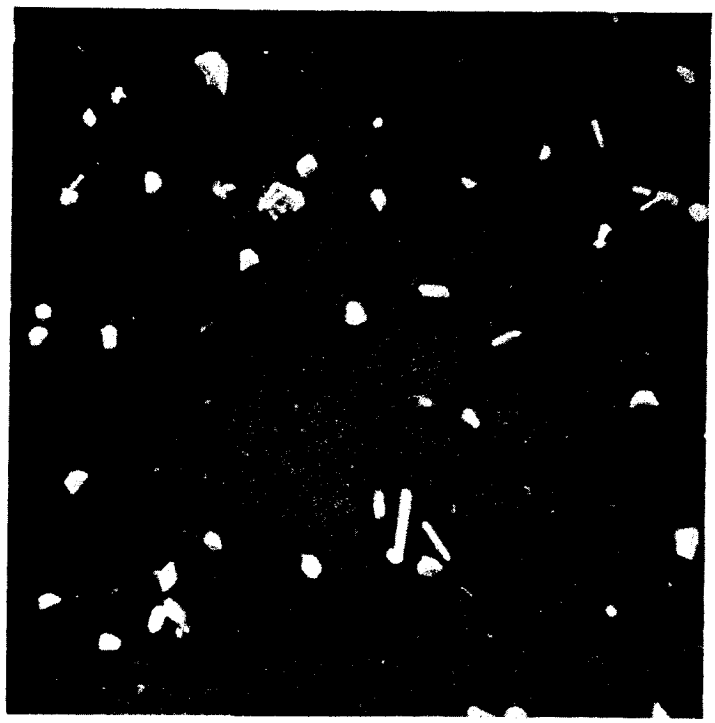


FIGURE 21. SILVER CRYSTALS CONDENSED ON SILICA TUBE WALLS (X 400)

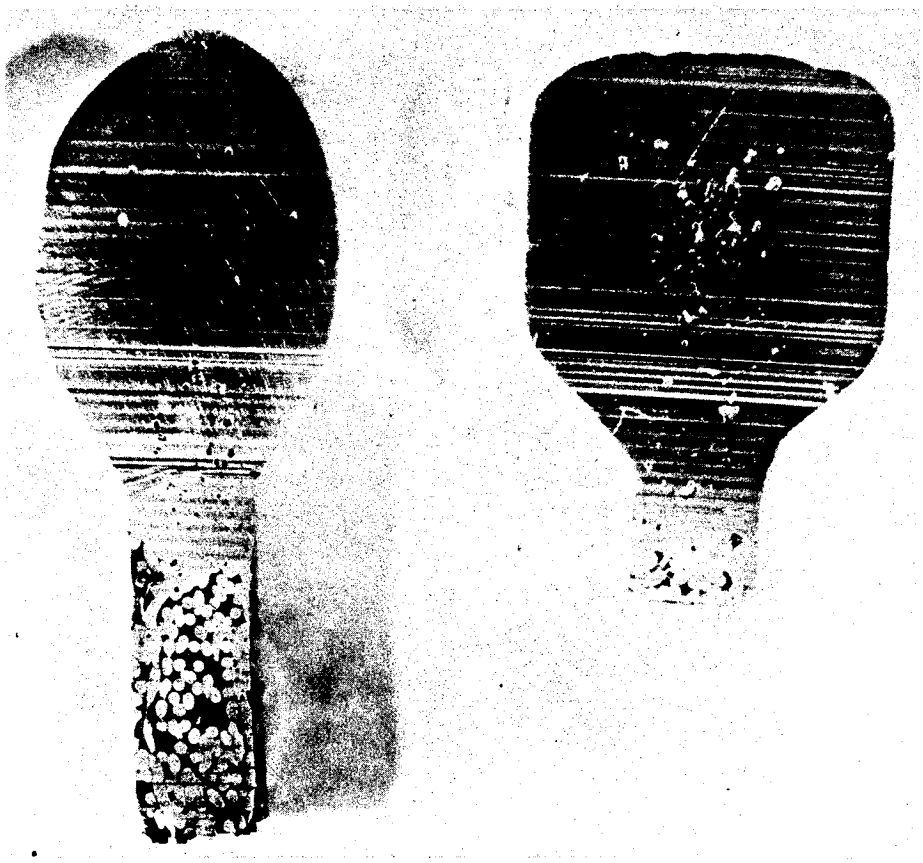


FIGURE 22. AS CUT SECTION THROUGH SKYLAB (LEFT) AND GROUND (RIGHT) SAMPLES (X 4).

FIGURE 23. POLISHED AND ETCHED SECTION THROUGH GROUND SAMPLES (X 9).

FIGURE 24. POLISHED SECTION THROUGH SKYLAB SAMPLE (X 6).

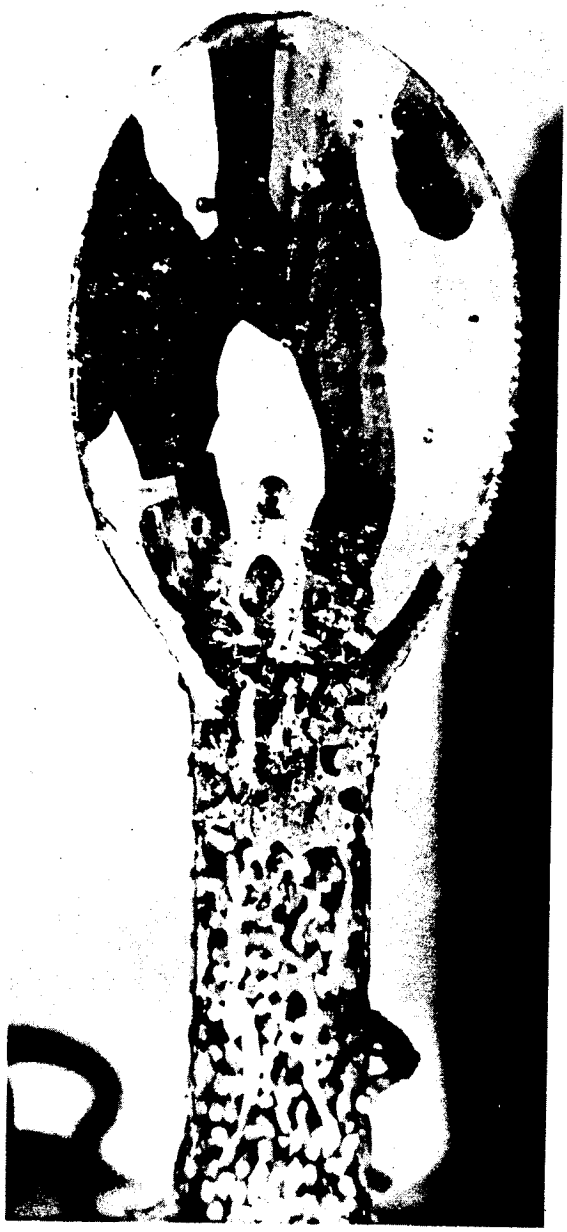


FIGURE 25. POLISHED AND ETCHED SECTION THROUGH SKYLAB SAMPLE (X 6).

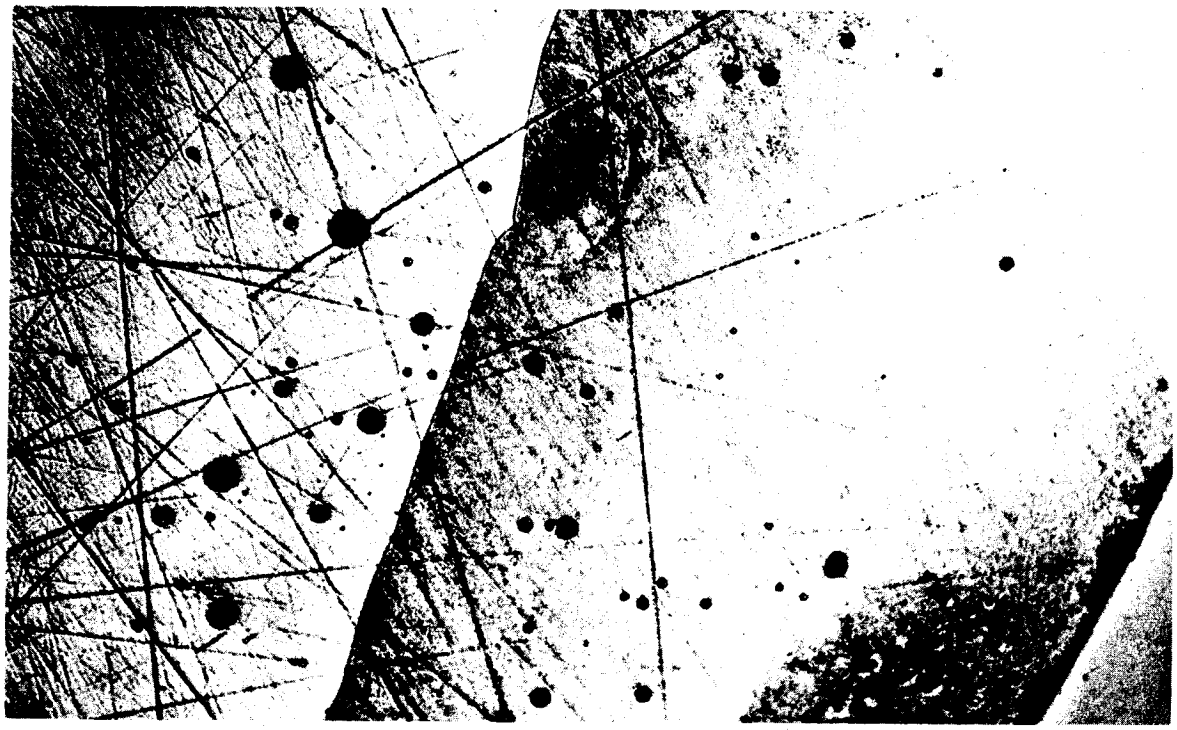


FIGURE 26. SMALL PORES IN SECTION OF SKYLAB SAMPLE (X 60).